

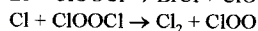
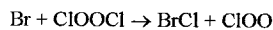
KINETICS OF ClOOCl REACTIONS

T. Ingham, S. P. Sander and R. R. Friedl

Jet Propulsion Laboratory

Background

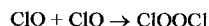
We have been studying the reactions of ClOOCl with Cl, Br and NO using the discharge-flow mass spectrometry technique.



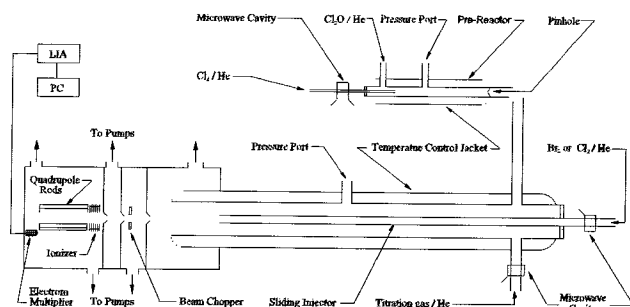
Our aim is to improve the kinetic database for reactions of ClOOCl with specific application to understanding the thermochemical properties of ClOOCl and modeling the chemistry of solid fuel rocket plumes and wakes. The reaction of ClOOCl with Br, in particular, represents a potentially useful method for calibrating ClO dimer concentrations by conversion to BrCl. We also have searched for other Br-containing products from this reaction to gain insight into the existence of non-peroxide forms of the ClO-dimer.

Experimental

Mass spectroscopy was used to detect ClOOCl and other molecular reaction products. ClOOCl was produced in a reactor sidearm from the reaction:



Atomic bromine and chlorine were generated in a movable injector tube. Their concentrations were in substantial excess over ClOOCl. Schematic of the apparatus is shown in Figure below.



Conclusions

Our work on these reactions has resulted in the first measurements of the temperature dependent kinetics of Cl and Br atom reactions with ClOOCl (see figure 1). Reaction rate coefficients of $k(\text{Cl}) = (7.60 \pm 0.28) \times 10^{-11} \exp((65 \pm 9)/T) \text{ cm}^3 \text{ s}^{-1}$ and $k(\text{Br}) = (5.88 \pm 0.24) \times 10^{-12} \exp((-173 \pm 10)/T) \text{ cm}^3 \text{ s}^{-1}$ were obtained. The Cl and Br reactions are thought to share a common direct Cl-atom abstraction mechanism involving significant long range charge transfer from ClOOCl to the incoming atom. The lower reaction rate for Br-atoms is consistent with the lower ionization potential for this atom relative to Cl-atoms, since stabilization of the transition state by electron delocalization from ClOOCl to the atom is diminished. In the case of the Cl-atom reaction, the long-range attractive potential effectively overcomes the reaction barrier and a small inverse temperature dependence is observed.

In the case of the Br-atom reaction, BrCl was identified as a major reaction product but its absolute yield could not be accurately determined. The absence of measurable amounts of BrO, Cl₂O and OClO reaction products supports the conclusion that BrCl is the sole Br-containing reaction product and suggests that our source of the ClO dimer (i.e. ClO + ClO) contains less than 10% of the non-peroxide forms ClClO₂ and ClOClO.

Finally, we have derived an upper limit of $1 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ for the NO reaction rate coefficient. The small value for the rate coefficient effectively rules out any interference from this reaction in recent ER-2 based measurements of polar stratospheric ClOOCl that

Results

Data were obtained at 1 torr total pressure in Helium buffer. Reaction kinetics and product data are shown in the following 4 figures.

Figure 2: Production of BrCl (open circles) and decay of ClOOCl (open squares) at 298 K.

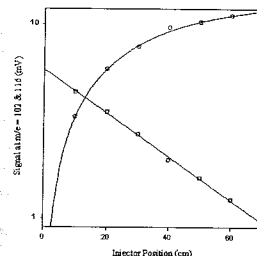


Figure 3: Observed Temperature dependence of Br + ClOOCl. Error bars encompass statistical scatter at the 95% confidence level and systematic error

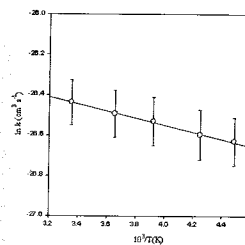


Figure 4: Temperature dependence of Cl + ClOOCl. Open squares and circles refer to different [Cl] calibration schemes. Error bars encompass statistical scatter at the 95% confidence level and systematic errors.

